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(71) Applicant: ROHM AND HAAS COMPANY

Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:

• Chaturvedi, Sanjay

Horsham, Pennsylvania 19044 (US)

• Gaffney, Anne Mae

West Chester, Pennsylvania 19380 (US)

• Han, Scott

Lawrenceville, New Jersey 08648 (US)

• Le, Dominique Hung Nhu

Upper Darby, Pennsylvania 19082 (US)

• Song, Ruozhi

Wilmington, Delaware 19809 (US)

• Heffner, Michele Doreen

Chalfont, Pennsylvania 18914 (US)

• Vickery, Elsie Mae

A3 Jenkintown, Pennsylvania 19046 (US)

(74) Representative: Kent, Venetia Katherine

Rohm and Haas (UK) Ltd

European Operations Patent Dept.

Lennig House

2 Mason's Avenue

Croydon, CR9 3NB (GB)

(54) **Promoted multi-metal oxide catalyst**

(57) A catalyst comprising a promoted mixed metal oxide is useful for the vapor phase oxidation of an alkane or a mixture of an alkane and an alkene to an unsaturated carboxylic acid and for the vapor phase ammoxidation of an alkane or a mixture of an alkane and an

alkene to an unsaturated nitrile. The multi-metal oxide catalyst comprises at least one element selected from the group consisting of Ni, Pd, Cu, Ag and Au.

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Description

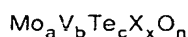
[0001] The present invention relates to an improved catalyst for the oxidation of alkanes or a mixture of alkanes and alkenes to their corresponding unsaturated carboxylic acids by vapor phase catalytic oxidation; to a method of making the catalyst; and to a process for the vapor phase catalytic oxidation of alkanes or a mixture of alkanes and alkenes to their corresponding unsaturated carboxylic acids.

[0002] The present invention also relates to a method of producing unsaturated nitriles by subjecting alkanes or a mixture of alkanes and alkenes to vapor phase catalytic oxidation in the presence of ammonia.

[0003] Nitriles, such as acrylonitrile and methacrylonitrile, have been industrially produced as important intermediates for the preparation of fibers, synthetic resins, synthetic rubbers, and the like. The most popular method for producing such nitriles is to subject an olefin such as propene or isobutene to a catalytic reaction with ammonia and oxygen in the presence of a catalyst in a gaseous phase at a high temperature. Known catalysts for conducting this reaction include a Mo-Bi-P-O catalyst, a V-Sb-O catalyst, an Sb-U-V-Ni-O catalyst, a Sb-Sn-O catalyst, a V-Sb-W-P-O catalyst and a catalyst obtained by mechanically mixing a V-Sb-W-O oxide and a Bi-Ce-Mo-W-O oxide. However, in view of the price difference between propane and propene or between isobutane and isobutene, attention has been drawn to the development of a method for producing acrylonitrile or methacrylonitrile by an ammoxidation reaction wherein a lower alkane, such as propane or isobutane, is used as a starting material, and it is catalytically reacted with ammonia and oxygen in a gaseous phase in the presence of a catalyst.

[0004] In particular, U.S. Patent No. 5,281,745 discloses a method for producing an unsaturated nitrile comprising subjecting an alkane and ammonia in the gaseous state to catalytic oxidation in the presence of a catalyst which satisfies the conditions:

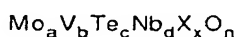
(1) the mixed metal oxide catalyst is represented by the empirical formula



wherein X is at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum, antimony, bismuth, boron and cerium and, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $x = 0.01$ to 1.0 and n is a number such that the total valency of the metal elements is satisfied; and

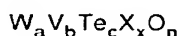
(2) the catalyst has X-ray diffraction peaks at the following angles ($\pm 0.3^\circ$) of 2θ in its X-ray diffraction pattern: 22.1° , 28.2° , 36.2° , 45.2° and 50.0° .

[0005] U.S. Patent No. 5,231,214 discloses a method of nitrile preparation comprising reacting an alkane in a gas phase contact reaction with ammonia in the presence of a mixed metal oxide catalyst of the formula



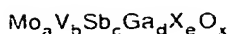
wherein X represents one or more elements selected from magnesium, calcium, strontium, barium, aluminum, gallium, thallium, indium, tin, zirconium, hafnium, tantalum, chromium, manganese, tungsten, iron, ruthenium, cobalt, rhodium, nickel, palladium, zinc, lead, arsenic, antimony, bismuth, lanthanum and cerium and when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0$ to 1.0 , $x = 0.0005$ to 1.0 and n is determined by the oxide form of the other elements.

[0006] Similarly, Japanese Laid-Open Patent Application Publication No. 6-228073 discloses a method of nitrile preparation comprising reacting an alkane in a gas phase contact reaction with ammonia in the presence of a mixed metal oxide catalyst of the formula



wherein X represents one or more elements selected from niobium, tantalum, titanium, aluminum, zirconium, chromium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum, antimony, bismuth, indium and cerium and, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $x = 0.01$ to 1.0 and n is determined by the oxide form of the elements.

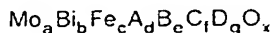
[0007] U.S. Patent No. 6,043,185 also discloses a catalyst useful in the manufacture of acrylonitrile or methacrylonitrile by the catalytic reaction in the vapor phase of a paraffin selected from propane and isobutane with molecular oxygen and ammonia by catalytic contact of the reactants in a reaction zone with a catalyst, wherein the catalyst has the empirical formula



where X is one or more of As, Te, Se, Nb, Ta, W, Ti, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, B, In, Ce, Re, Ir, Ge, Sn, Bi, Y, Pr, an alkali metal and an alkaline earth metal; and when $a = 1$, $b = 0.0$ to 0.99 , $c = 0.01$ to 0.9 , $d = 0.01$ to 0.5 , $e = 0.0$ to 1.0 and x is determined by the oxidation state of the cations present.

[0008] Unsaturated carboxylic acids such as acrylic acid and methacrylic acid are industrially important as starting materials for various synthetic resins, coating materials and plasticizers. Commercially, the current process for acrylic acid manufacture involves a two-step catalytic oxidation reaction starting with a propene feed. In the first stage, propene is converted to acrolein over a modified bismuth molybdate catalyst. In the second stage, acrolein product from the first stage is converted to acrylic acid using a catalyst composed of mainly molybdenum and vanadium oxides. In most cases, the catalyst formulations are proprietary to the catalyst supplier, but the technology is well established. Moreover, there is an incentive to develop a single step process to prepare the unsaturated acid from its corresponding alkene. Therefore, the prior art describes cases where complex metal oxide catalysts are utilized for the preparation of unsaturated acid from a corresponding alkene in a single step.

[0009] European Published Patent Application No. 0 630 879 B1 discloses a process for producing an unsaturated aldehyde and a carboxylic acid which comprises subjecting propene, isobutene or tertiary butanol to gas phase catalytic oxidation with molecular oxygen in the presence of (i) a catalyst composite oxide represented by the formula

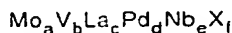


wherein A represents Ni and/or Co, B represents at least one element selected from Mn, Zn, Ca, Mg, Sn and Pb, C represents at least one element selected from P, B, As, Te, W, Sb and Si, and D represents at least one element selected from K, Rb, Cs and Tl; and

wherein, when $a = 12$, $0 < b \leq 10$, $0 < c \leq 10$, $1 \leq d \leq 10$, $0 \leq e \leq 10$, $0 \leq f \leq 20$ and $0 \leq g \leq 2$, and x has a value dependent on the oxidation state of the other elements; and (ii) a molybdenum oxide which in itself is substantially inert to said gas phase catalytic oxidation to provide the corresponding unsaturated aldehyde and unsaturated carboxylic acid.

[0010] Japanese Laid-Open Patent Application Publication No. 07-053448 discloses the manufacture of acrylic acid by the gas-phase catalytic oxidation of propene in the presence of mixed metal oxides containing Mo, V, Te, O and X wherein X is at least one of Nb, Ta, W, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pd, Pt, Sb, Bi, B, In, Li, Na, K, Rb, Cs and Ce.

[0011] Published International Application No. WO 00/09260 discloses a catalyst for selective oxidation of propene to acrylic acid and acrolein containing a catalyst composition comprising the elements Mo, V, La, Pd, Nb and X in the following ratio:



wherein X is Cu or Cr or a mixture thereof,

a is 1,

b is 0.01 to 0.9,

c is >0 to 0.2

d is 0.0000001 to 0.2,

e is 0 to 0.2, and

f is 0 to 0.2; and

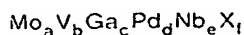
wherein the numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, La, Pd, Nb and X, respectively, in the catalyst and the elements are present in combination with oxygen.

[0012] Commercial incentives also exist for producing acrylic acid using a lower cost propane feed. Therefore, the prior art describes cases wherein a mixed metal oxide catalyst is used to convert propane to acrylic acid in one step.

[0013] U.S. Patent No. 5,380,933 discloses a method for producing an unsaturated carboxylic acid comprising subjecting an alkane to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing a mixed metal oxide comprising, as essential components, Mo, V, Te, O and X, wherein X is at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, ruthenium, cobalt, rhodium, nickel, palladium, platinum, antimony, bismuth, boron, indium and cerium; and wherein the proportions of the respective essential components, based on the total amount of the essential components, exclusive of oxygen, satisfy the following relationships:

$0.25 < r(\text{Mo}) < 0.98$, $0.003 < r(\text{V}) < 0.5$, $0.003 < r(\text{Te}) < 0.5$ and $0.003 < r(\text{X}) < 0.5$, wherein $r(\text{Mo})$, $r(\text{V})$, $r(\text{Te})$ and $r(\text{X})$ are the molar fractions of Mo, V, Te and X, respectively, based on the total amount of the essential components exclusive of oxygen.

[0014] Published International Application No. WO 00/29106 discloses a catalyst for selective oxidation of propane to oxygenated products including acrylic acid, acrolein and acetic acid, said catalyst system containing a catalyst composition comprising



wherein X is at least one element selected from La, Te, Ge, Zn, Si, In and W.

a is 1,

b is 0.01 to 0.9,

c is >0 to 0.2,

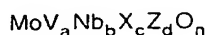
d is 0.0000001 to 0.2,

e is >0 to 0.2, and

f is .0 to 0.5; and

wherein the numerical values of a, b, c, d, e and f represent the relative gram-atom ratios of the elements Mo, V, Ga, Pd, Nb and X, respectively, in the catalyst and the elements are present in combination with oxygen.

[0015] Japanese Laid-Open Patent Application Publication No. 2000-037623 discloses a method for producing an unsaturated carboxylic acid comprising subjecting an alkane to a vapor phase catalytic oxidation in the presence of a catalyst having the empirical formula

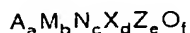


wherein X is at least one element selected from the group consisting of Te and Sb, Z is at least one element selected from the group consisting of W, Cr, Ta, Ti, Zr, Hf, Mn, Re, Fe, Ru, Co, Rh, Ni, Pd, Pt, Ag, Zn, B, Al, Ga, In, Ge, Sn, Pb, P, Bi, Y, rare earth elements and alkaline earth elements, $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.01 \leq c \leq 1.0$, $0 \leq d \leq 1.0$ and n is determined by the oxidation states of the other elements.

[0016] Despite the above-noted attempts to provide new and improved catalysts for the oxidation of alkanes to unsaturated carboxylic acids and for the ammoxidation of alkanes to unsaturated nitriles, one impediment to the provision of a commercially viable process for such catalytic oxidations is the identification of a catalyst providing adequate conversion and suitable selectivity, thereby providing sufficient yield of the unsaturated product.

[0017] By the present invention, there are provided promoted catalysts wherein the activity is greatly enhanced as to the base catalyst and, hence, the overall yield of the desired reaction product is also greatly enhanced.

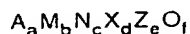
[0018] Thus, in a first aspect, the present invention provides a catalyst comprising a promoted mixed metal oxide having the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and

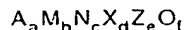
wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

[0019] In a second aspect, the present invention provides a process for producing an unsaturated carboxylic acid, which comprises subjecting an alkane or a mixture of an alkane and an alkene to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing a promoted mixed metal oxide having the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

[0020] In a third aspect, the present invention provides a process for producing an unsaturated nitrile, which comprises subjecting an alkane, or a mixture of an alkane and an alkene, and ammonia to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing a promoted mixed metal oxide having the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

[0021] In a fourth aspect, the present invention provides a catalyst produced by the process comprising:

- (1) admixing compounds of the elements A, M, N, X and Z and at least one solvent to form an admixture, wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au, and wherein the elements A, M, N, X and Z are present in such amounts that the atomic ratio of A:M:N:X:Z is $1 : 0.01$ to $1.0 : 0.01$ to $1.0 : 0.01$ to $1.0 : 0.001$ to 0.1 ;
- (2) removing said at least one solvent from the admixture to obtain a catalyst precursor; and
- (3) calcining said catalyst precursor.

[0022] In a fifth aspect, the present invention provides a process for producing an unsaturated carboxylic acid, which comprises subjecting an alkane or a mixture of an alkane and an alkene to a vapor phase catalytic oxidation reaction in the presence of the catalyst produced by the process comprising:

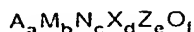
- (1) admixing compounds of the elements A, M, N, X and Z and at least one solvent to form an admixture, wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au, and wherein the elements A, M, N, X and Z are present in such amounts that the atomic ratio of A:M:N:X:Z is $1 : 0.01$ to $1.0 : 0.01$ to $1.0 : 0.01$ to $1.0 : 0.001$ to 0.1 ;
- (2) removing said at least one solvent from the admixture to obtain a catalyst precursor; and
- (3) calcining said catalyst precursor.

[0023] In a sixth aspect, the present invention provides a process for producing an unsaturated nitrile, which comprises subjecting an alkane, or a mixture of an alkane and an alkene, and ammonia to a vapor phase catalytic oxidation reaction in the presence of the catalyst produced by the process comprising:

- (1) admixing compounds of the elements A, M, N, X and Z and at least one solvent to form an admixture, wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au, and wherein the elements A, M, N, X and Z

are present in such amounts that the atomic ratio of A:M:N:X:Z is 1 : 0.01 to 1.0:0.01 to 1.0:0.01 to 1.0:0.001 to 0.1;
 (2) removing said at least one solvent from the admixture to obtain a catalyst precursor; and
 (3) calcining said catalyst precursor.

[0024] The promoted mixed metal oxide to be used as a catalyst component of the present invention has the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

[0025] Preferably, when $a = 1$, $b = 0.1$ to 0.5 , $c = 0.05$ to 0.5 , $d = 0.01$ to 0.5 and $e = 0.002$ to 0.04 . More preferably, when $a = 1$, $b = 0.15$ to 0.45 , $c = 0.05$ to 0.45 , $d = 0.01$ to 0.1 and $e = 0.002$ to 0.01 . The value of f , i.e. the amount of oxygen present, is dependent on the oxidation state of the other elements in the catalyst. However, f is typically in the range of from 3 to 4.7.

[0026] Preferred promoted mixed metal oxides have the empirical formulae $Mo_a V_b Te_c Nb_d Z_e O_f$ and $W_a V_b Te_c Nb_d Z_e O_f$ wherein Z, a, b, c, d, e and f are as previously defined.

[0027] Further, as the promoted mixed metal oxide, one having a certain specific crystal structure is preferred. Specifically, preference is given to the one which exhibits the following five main diffraction peaks at specific diffraction angles 2θ in the X-ray diffraction pattern of the promoted mixed metal oxide (as measured using Cu-K α radiation as the source):

| X-ray lattice plane | | |
|---|---------------------------------|--------------------|
| Diffraction angle 2θ ($\pm 0.3^\circ$) | Spacing medium (\AA) | Relative intensity |
| 22.1° | 4.02 | 100 |
| 28.2° | 3.16 | 20~150 |
| 36.2° | 2.48 | 5~60 |
| 45.2° | 2.00 | 2~40 |
| 50.0° | 1.82 | 2~40 |

[0028] The intensity of the X-ray diffraction peaks may vary upon the measuring of each crystal. However, the intensity, relative to the peak intensity at 22.1° being 100, is usually within the above ranges. Generally, the peak intensities at $2\theta = 22.1^\circ$ and 28.2° are distinctly observed. However, so long as the above five diffraction peaks are observable, the basic crystal structure is the same even if other peaks are observed in addition to the five diffraction peaks, and such a structure is useful for the present invention.

[0029] The promoted mixed metal oxide can be prepared in the following manner.

[0030] In a first step a slurry or solution may be formed by admixing metal compounds, preferably at least one of which contains oxygen, and at least one solvent in appropriate amounts to form the slurry or solution. Preferably, a solution is formed at this stage of the catalyst preparation. Generally, the metal compounds contain elements A, M, N, X, Z and O, as previously defined.

[0031] Suitable solvents include water; alcohols including, but not limited to, methanol, ethanol, propanol, and diols, etc.; as well as other polar solvents known in the art. Generally, water is preferred. The water is any water suitable for use in chemical syntheses including, without limitation, distilled water and de-ionized water. The amount of water present is preferably an amount sufficient to keep the elements substantially in solution long enough to avoid or minimize compositional and/or phase segregation during the preparation steps. Accordingly, the amount of water will vary according to the amounts and solubilities of the materials combined. However, as stated above, the amount of water is preferably sufficient to ensure an aqueous solution is formed, and not a slurry, at the time of mixing.

[0032] For example, when a mixed metal oxide of the formula $Mo_a V_b Te_c Nb_d Au_e O_f$ wherein the element A is Mo, the element M is V, the element N is Te and the element X is Nb, is to be prepared, an aqueous solution of niobium oxalate may be added to an aqueous solution or slurry of ammonium heptamolybdate, ammonium metavanadate, telluric acid

and ammonium tetrachloroaurate, so that the atomic ratio of the respective metal elements would be in the prescribed proportions.

[0033] Once the aqueous slurry or solution (preferably a solution) is formed, the water is removed by any suitable method, known in the art, to form a catalyst precursor. Such methods include, without limitation, vacuum drying, freeze drying, spray drying, rotary evaporation and air drying. Vacuum drying is generally performed at pressures ranging from 10mmHg to 500mmHg. Freeze drying typically entails freezing the slurry or solution, using, for instance, liquid nitrogen, and drying the frozen slurry or solution under vacuum. Spray drying is generally performed under an inert atmosphere such as nitrogen or argon, with an inlet temperature ranging from 125°C to 200°C and an outlet temperature ranging from 75°C to 150°C. Rotary evaporation is generally performed at a bath temperature of from 25°C to 90°C and at a pressure of from 10mmHg to 760mmHg, preferably at a bath temperature of from 40° to 90°C and at a pressure of from 10mmHg to 350mmHg, more preferably at a bath temperature of from 40°C to 60°C and at a pressure of from 10mmHg to 40mmHg. Air drying may be effected at temperatures ranging from 25°C to 90°C. Rotary evaporation or air drying are generally preferred.

[0034] Once obtained, the catalyst precursor is calcined. The calcination may be conducted in an oxygen-containing atmosphere or in the substantial absence of oxygen, e.g., in an inert atmosphere or in vacuo. The inert atmosphere may be any material which is substantially inert, i.e., does not react or interact with, the catalyst precursor. Suitable examples include, without limitation, nitrogen, argon, xenon, helium or mixtures thereof. Preferably, the inert atmosphere is argon or nitrogen. The inert atmosphere may flow over the surface of the catalyst precursor or may not flow thereover (a static environment). When the inert atmosphere does flow over the surface of the catalyst precursor, the flow rate can vary over a wide range, e.g., at a space velocity of from 1 to 500 hr⁻¹.

[0035] The calcination is usually performed at a temperature of from 350°C to 850°C, preferably from 400°C to 700°C, more preferably from 500°C to 640°C. The calcination is performed for an amount of time suitable to form the aforementioned catalyst. Typically, the calcination is performed for from 0.5 to 30 hours, preferably from 1 to 25 hours, more preferably for from 1 to 15 hours, to obtain the desired promoted mixed metal oxide.

[0036] In a preferred mode of operation, the catalyst precursor is calcined in two stages. In the first stage, the catalyst precursor is calcined in an oxidizing environment (e.g. air) at a temperature of from 200°C to 400°C, preferably from 275°C to 325°C for from 15 minutes to 8 hours, preferably for from 1 to 3 hours. In the second stage, the material from the first stage is calcined in a non-oxidizing environment (e.g., an inert atmosphere) at a temperature of from 500°C to 750°C, preferably for from 550°C to 650°C, for 15 minutes to 8 hours, preferably for from 1 to 3 hours. Optionally, a reducing gas, such as, for example, ammonia or hydrogen, may be added during the second stage calcination.

[0037] In a particularly preferred mode of operation, the catalyst precursor in the first stage is placed in the desired oxidizing atmosphere at room temperature and then raised to the first stage calcination temperature and held there for the desired first stage calcination time. The atmosphere is then replaced with the desired non-oxidizing atmosphere for the second stage calcination, the temperature is raised to the desired second stage calcination temperature and held there for the desired second stage calcination time.

[0038] Although any type of heating mechanism, e.g., a furnace, may be utilized during the calcination, it is preferred to conduct the calcination under a flow of the designated gaseous environment. Therefore, it is advantageous to conduct the calcination in a bed with continuous flow of the desired gas(es) through the bed of solid catalyst precursor particles.

[0039] With calcination, a catalyst is formed having the formula $A_aM_bN_cX_dZ_eO_f$ wherein A, M, N, X, Z, O, a, b, c, d, e and f are as previously defined.

[0040] The starting materials for the above promoted mixed metal oxide are not limited to those described above. A wide range of materials including, for example, oxides, nitrates, halides or oxyhalides, alkoxides, acetylacetonates, and organometallic compounds may be used. For example, ammonium heptamolybdate may be utilized for the source of molybdenum in the catalyst. However, compounds such as MoO₃, MoO₂, MoCl₅, MoOCl₄, Mo(OC₂H₅)₅, molybdenum acetylacetonate, phosphomolybdic acid and silicomolybdic acid may also be utilized instead of ammonium heptamolybdate. Similarly, ammonium metavanadate may be utilized for the source of vanadium in the catalyst. However, compounds such as V₂O₅, V₂O₃, VOCl₃, VCl₄, VO(OC₂H₅)₃, vanadium acetylacetonate and vanadyl acetylacetonate may also be utilized instead of ammonium metavanadate. The tellurium source may include telluric acid, TeCl₄, Te(OC₂H₅)₅, Te(OCH(CH₃)₂)₄ and TeO₂. The niobium source may include ammonium niobium oxalate, Nb₂O₅, NbCl₅, niobic acid or Nb(OC₂H₅)₅ as well as the more conventional niobium oxalate. The nickel source may include nickel(II) acetate tetrahydrate, Ni(NO₃)₂, nickel(II) oxalate, NiO, Ni(OH)₂, NiCl₂, NiBr₂, nickel(II) acetylacetonate, nickel(II) sulfate, NiS or nickel metal. The palladium source may include Pd(NO₃)₂, palladium(II) acetate, palladium oxalate, PdO, Pd(OH)₂, PdCl₂, palladium acetylacetonate or palladium metal. The copper source may be copper acetate, copper acetate monohydrate, copper acetate hydrate, copper acetylacetonate, copper bromide, copper carbonate, copper chloride, copper chloride dihydrate, copper fluoride, copper formate hydrate, copper gluconate, copper hydroxide, copper iodide, copper methoxide, copper nitrate, copper nitrate hydrate, copper oxide, copper tartrate hydrate or a solution of copper in an aqueous inorganic acid, e.g., nitric acid. The silver source may be silver acetate, silver acetylacetonate, silver benzoate, silver bromide, silver carbonate, silver chloride, silver citrate hydrate, silver fluoride, silver

iodide, silver lactate, silver nitrate, silver nitrite, silver oxide, silver phosphate or a solution of silver in an aqueous inorganic acid, e.g., nitric acid. The gold source may be ammonium tetrachloroaurate, gold bromide, gold chloride, gold cyanide, gold hydroxide, gold iodide, gold oxide, gold trichloride acid and gold sulfide.

[0041] A promoted mixed metal oxide, thus obtained, exhibits excellent catalytic activities by itself. However, the promoted mixed metal oxide can be converted to a catalyst having higher activities by grinding.

[0042] There is no particular restriction as to the grinding method, and conventional methods may be employed. As a dry grinding method, a method of using a gas stream grinder may, for example, be mentioned wherein coarse particles are permitted to collide with one another in a high speed gas stream for grinding. The grinding may be conducted not only mechanically but also by using a mortar or the like in the case of a small scale operation.

[0043] As a wet grinding method wherein grinding is conducted in a wet state by adding water or an organic solvent to the above mixed metal oxide, a conventional method of using a rotary cylinder-type medium mill or a medium-stirring type mill, may be mentioned. The rotary cylinder-type medium mill is a wet mill of the type wherein a container for the object to be ground is rotated, and it includes, for example, a ball mill and a rod mill. The medium-stirring type mill is a wet mill of the type wherein the object to be ground, contained in a container is stirred by a stirring apparatus, and it includes, for example, a rotary screw type mill, and a rotary disc type mill.

[0044] The conditions for grinding may suitably be set to meet the nature of the above-mentioned promoted mixed metal oxide, the viscosity, the concentration, etc. of the solvent used in the case of wet grinding, or the optimum conditions of the grinding apparatus. However, it is preferred that grinding is conducted until the average particle size of the ground catalyst precursor would usually be at most 20 μ m, more preferably at most 5 μ m. Improvement in the catalytic performance may occur due to such grinding.

[0045] Further, in some cases, it is possible to further improve the catalytic activities by further adding a solvent to the ground catalyst precursor to form a solution or slurry, followed by drying again. There is no particular restriction as to the concentration of the solution or slurry, and it is usual to adjust the solution or slurry so that the total amount of the starting material compounds for the ground catalyst precursor is from 10 to 60 wt %. Then, this solution or slurry is dried by a method such as spray drying, freeze drying, evaporation to dryness or vacuum drying, preferably by the spray drying method. Further, similar drying may be conducted also in the case where wet grinding is conducted.

[0046] The oxide obtained by the above-mentioned method may be used as a final catalyst, but it may further be subjected to heat treatment usually at a temperature of from 200° to 700°C for from 0.1 to 10 hours.

[0047] The promoted mixed metal oxide thus obtained may be used by itself as a solid catalyst, but may be formed into a catalyst together with a suitable carrier such as silica, alumina, titania, aluminosilicate, diatomaceous earth or zirconia. Further, it may be molded into a suitable shape and particle size depending upon the scale or system of the reactor.

[0048] Alternatively, the metal components of the presently contemplated catalyst may be supported on materials such as alumina, silica, silica-alumina, zirconia, titania, etc. by conventional incipient wetness techniques. In one typical method, solutions containing the metals are contacted with the dry support such that the support is wetted; then, the resultant wetted material is dried, for example, at a temperature from room temperature to 200°C followed by calcination as described above. In another method, metal solutions are contacted with the support, typically in volume ratios of greater than 3 : 1 (metal solution : support), and the solution agitated such that the metal ions are ion-exchanged onto the support. The metal-containing support is then dried and calcined as detailed above.

[0049] In its second aspect, the present invention provides a process for producing an unsaturated carboxylic acid, which comprises subjecting an alkane, or a mixture of an alkane and an alkene, to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing the above promoted mixed metal oxide, to produce an unsaturated carboxylic acid.

[0050] In the production of such an unsaturated carboxylic acid, it is preferred to employ a starting material gas which contains steam. In such a case, as a starting material gas to be supplied to the reaction system, a gas mixture comprising a steam-containing alkane, or a steam-containing mixture of alkane and alkene, and an oxygen-containing gas, is usually used. However, the steam-containing alkane, or the steam-containing mixture of alkane and alkene, and the oxygen-containing gas may be alternately supplied to the reaction system. The steam to be employed may be present in the form of steam gas in the reaction system, and the manner of its introduction is not particularly limited.

[0051] Further, as a diluting gas, an inert gas such as nitrogen, argon or helium may be supplied. The molar ratio (alkane or mixture of alkane and alkene) : (oxygen) : (diluting gas) : (H₂O) in the starting material gas is preferably (1) : (0.1 to 10) : (0 to 20) : (0.2 to 70), more preferably (1) : (1 to 5.0) : (0 to 10) : (5 to 40).

[0052] When steam is supplied together with the alkane, or the mixture of alkane and alkene, as starting material gas, the selectivity for an unsaturated carboxylic acid is distinctly improved, and the unsaturated carboxylic acid can be obtained from the alkane, or mixture of alkane and alkene, in good yield simply by contacting in one stage. However, the conventional technique utilizes a diluting gas such as nitrogen, argon or helium for the purpose of diluting the starting material. As such a diluting gas, to adjust the space velocity, the oxygen partial pressure and the steam partial pressure, an inert gas such as nitrogen, argon or helium may be used together with the steam.

[0053] As the starting material alkane it is preferred to employ a C_{3-8} alkane, particularly propane, isobutane or n-butane; more preferably, propane or isobutane; most preferably, propane. According to the present invention, from such an alkane, an unsaturated carboxylic acid such as an α,β -unsaturated carboxylic acid can be obtained in good yield. For example, when propane or isobutane is used as the starting material alkane, acrylic acid or methacrylic acid will be obtained, respectively, in good yield.

[0054] In the present invention, as the starting material mixture of alkane and alkene, it is preferred to employ a mixture of C_{3-8} alkane and C_{3-8} alkene, particularly propane and propene, isobutane and isobutene or n-butane and n-butene. As the starting material mixture of alkane and alkene, propane and propene or isobutane and isobutene are more preferred. Most preferred is a mixture of propane and propene. According to the present invention, from such a mixture of an alkane and an alkene, an unsaturated carboxylic acid such as an α,β -unsaturated carboxylic acid can be obtained in good yield. For example, when propane and propene or isobutane and isobutene are used as the starting material mixture of alkane and alkene, acrylic acid or methacrylic acid will be obtained, respectively, in good yield. Preferably, in the mixture of alkane and alkene, the alkene is present in an amount of at least 0.5% by weight, more preferably at least 1.0% by weight to 95% by weight; most preferably, 3% by weight to 90% by weight.

[0055] As an alternative, an alkanol, such as isobutanol, which will dehydrate under the reaction conditions to form its corresponding alkene, i.e. isobutene, may also be used as a feed to the present process or in conjunction with the previously mentioned feed streams.

[0056] The purity of the starting material alkane is not particularly limited, and an alkane containing a lower alkane such as methane or ethane, air or carbon dioxide, as impurities, may be used without any particular problem. Further, the starting material alkane may be a mixture of various alkanes. Similarly, the purity of the starting material mixture of alkane and alkene is not particularly limited, and a mixture of alkane and alkene containing a lower alkene such as ethene, a lower alkane such as methane or ethane, air or carbon dioxide, as impurities, may be used without any particular problem. Further, the starting material mixture of alkane and alkene may be a mixture of various alkanes and alkenes.

[0057] There is no limitation on the source of the alkene. It may be purchased, per se, or in admixture with an alkane and/or other impurities. Alternatively, it can be obtained as a byproduct of alkane oxidation. Similarly, there is no limitation on the source of the alkane. It may be purchased, per se, or in admixture with an alkene and/or other impurities. Moreover, the alkane, regardless of source, and the alkene, regardless of source, may be blended as desired.

[0058] The detailed mechanism of the oxidation reaction of the present invention is not clearly understood, but the oxidation reaction is carried out by oxygen atoms present in the above promoted mixed metal oxide or by molecular oxygen present in the feed gas. To incorporate molecular oxygen into the feed gas, such molecular oxygen may be pure oxygen gas. However, it is usually more economical to use an oxygen-containing gas such as air, since purity is not particularly required.

[0059] It is also possible to use only an alkane, or a mixture of alkane and alkene, substantially in the absence of molecular oxygen for the vapor phase catalytic reaction. In such a case, it is preferred to adopt a method wherein a part of the catalyst is appropriately withdrawn from the reaction zone from time to time, then sent to an oxidation regenerator, regenerated and then returned to the reaction zone for reuse. As the regeneration method of the catalyst, a method may, for example, be mentioned which comprises contacting an oxidative gas such as oxygen, air or nitrogen monoxide with the catalyst in the regenerator usually at a temperature of from 300° to 600°C.

[0060] The second aspect of the present invention will be described in further detail with respect to a case where propane is used as the starting material alkane and air is used as the oxygen source. The reaction system may be a fixed bed system or a fluidized bed system. However, since the reaction is an exothermic reaction, a fluidized bed system may preferably be employed whereby it is easy to control the reaction temperature. The proportion of air to be supplied to the reaction system is important for the selectivity for the resulting acrylic acid, and it is usually at most 25 moles, preferably from 0.2 to 18 moles per mole of propane, whereby high selectivity for acrylic acid can be obtained. This reaction can be conducted usually under atmospheric pressure, but may be conducted under a slightly elevated pressure or slightly reduced pressure. With respect to other alkanes such as isobutane, or to mixtures of alkanes and alkenes such as propane and propene, the composition of the feed gas may be selected in accordance with the conditions for propane.

[0061] Typical reaction conditions for the oxidation of propane or isobutane to acrylic acid or methacrylic acid may be utilized in the practice of the present invention. The process may be practiced in a single pass mode (only fresh feed is fed to the reactor) or in a recycle mode (at least a portion of the reactor effluent is returned to the reactor). General conditions for the process of the present invention are as follows: the reaction temperature can vary from 200°C to 700°C, but is usually in the range of from 200°C to 550°C, more preferably 250°C to 480°C, most preferably 300°C to 400°C; the gas space velocity, SV, in the vapor phase reaction is usually within a range of from 100 to 10,000 hr^{-1} , preferably 300 to 6,000 hr^{-1} , more preferably 300 to 2,000 hr^{-1} ; the average contact time with the catalyst can be from 0.01 to 10 seconds or more, but is usually in the range of from 0.1 to 10 seconds, preferably from 2 to 6 seconds; the pressure in the reaction zone usually ranges from 0 to 75 psig, but is preferably no more than 50 psig. In a single

pass mode process, it is preferred that the oxygen be supplied from an oxygen-containing gas such as air. The single pass mode process may also be practiced with oxygen addition. In the practice of the recycle mode process, oxygen gas by itself is the preferred source so as to avoid the build up of inert gases in the reaction zone.

[0062] Of course, in the oxidation reaction of the present invention, it is important that the hydrocarbon and oxygen concentrations in the feed gases be maintained at the appropriate levels to minimize or avoid entering a flammable regime within the reaction zone or especially at the outlet of the reactor zone. Generally, it is preferred that the outlet oxygen levels be low to both minimize after-burning and, particularly, in the recycle mode of operation, to minimize the amount of oxygen in the recycled gaseous effluent stream. In addition, operation of the reaction at a low temperature (below 450°C) is extremely attractive because after-burning becomes less of a problem which enables the attainment of higher selectivity to the desired products. The catalyst of the present invention operates more efficiently at the lower temperature range set forth above, significantly reducing the formation of acetic acid and carbon oxides, and increasing selectivity to acrylic acid. As a diluting gas to adjust the space velocity and the oxygen partial pressure, an inert gas such as nitrogen, argon or helium may be employed.

[0063] When the oxidation reaction of propane, and especially the oxidation reaction of propane and propene, is conducted by the method of the present invention, carbon monoxide, carbon dioxide, acetic acid, etc. may be produced as by-products, in addition to acrylic acid. Further, in the method of the present invention, an unsaturated aldehyde may sometimes be formed depending upon the reaction conditions. For example, when propane is present in the starting material mixture, acrolein may be formed; and when isobutane is present in the starting material mixture, methacrolein may be formed. In such a case, such an unsaturated aldehyde can be converted to the desired unsaturated carboxylic acid by subjecting it again to the vapor phase catalytic oxidation with the promoted mixed metal oxide-containing catalyst of the present invention or by subjecting it to a vapor phase catalytic oxidation reaction with a conventional oxidation reaction catalyst for an unsaturated aldehyde.

[0064] In its third aspect, the method of the present invention comprises subjecting an alkane, or a mixture of an alkane and an alkene, to a vapor phase catalytic oxidation reaction with ammonia in the presence of a catalyst containing the above mixed metal oxide, to produce an unsaturated nitrile.

[0065] In the production of such an unsaturated nitrile, as the starting material alkane, it is preferred to employ a C₃₋₈alkane such as propane, butane, isobutane, pentane, hexane and heptane. However, in view of the industrial application of nitriles to be produced, it is preferred to employ a lower alkane having 3 or 4 carbon atoms, particularly propane and isobutane.

[0066] Similarly, as the starting material mixture of alkane and alkene, it is preferred to employ a mixture of C₃₋₈alkane and C₃₋₈alkene such as propane and propene, butane and butene, isobutane and isobutene, pentane and pentene, hexane and hexene, and heptane and heptene. However, in view of the industrial application of nitriles to be produced, it is more preferred to employ a mixture of a lower alkane having 3 or 4 carbon atoms and a lower alkene having 3 or 4 carbon atoms, particularly propane and propene or isobutane and isobutene. Preferably, in the mixture of alkane and alkene, the alkene is present in an amount of at least 0.5% by weight, more preferably at least 1.0% by weight to 95% by weight, most preferably 3% by weight to 90% by weight.

[0067] The purity of the starting material alkane is not particularly limited, and an alkane containing a lower alkane such as methane or ethane, air or carbon dioxide, as impurities, may be used without any particular problem. Further, the starting material alkane may be a mixture of various alkanes. Similarly, the purity of the starting material mixture of alkane and alkene is not particularly limited, and a mixture of alkane and alkene containing a lower alkene such as ethene, a lower alkane such as methane or ethane, air or carbon dioxide, as impurities, may be used without any particular problem. Further, the starting material mixture of alkane and alkene may be a mixture of various alkanes and alkenes.

[0068] There is no limitation on the source of the alkene. It may be purchased, per se, or in admixture with an alkane and/or other impurities. Alternatively, it can be obtained as a byproduct of alkane oxidation. Similarly, there is no limitation on the source of the alkane. It may be purchased, per se, or in admixture with an alkene and/or other impurities. Moreover, the alkane, regardless of source, and the alkene, regardless of source, may be blended as desired.

[0069] The detailed mechanism of the ammoxidation reaction of this aspect of the present invention is not clearly understood. However, the oxidation reaction is conducted by the oxygen atoms present in the above promoted mixed metal oxide or by the molecular oxygen in the feed gas. When molecular oxygen is incorporated in the feed gas, the oxygen may be pure oxygen gas. However, since high purity is not required, it is usually economical to use an oxygen-containing gas such as air.

[0070] As the feed gas, it is possible to use a gas mixture comprising an alkane, or a mixture of an alkane and an alkene, ammonia and an oxygen-containing gas. However, a gas mixture comprising an alkane or a mixture of an alkane and an alkene and ammonia, and an oxygen-containing gas may be supplied alternately.

[0071] When the gas phase catalytic reaction is conducted using an alkane, or a mixture of an alkane and an alkene, and ammonia substantially free from molecular oxygen, as the feed gas, it is advisable to employ a method wherein a part of the catalyst is periodically withdrawn and sent to an oxidation regenerator for regeneration, and the regenerated

catalyst is returned to the reaction zone. As a method for regenerating the catalyst, a method may be mentioned wherein an oxidizing gas such as oxygen, air or nitrogen monoxide is permitted to flow through the catalyst in the regenerator usually at a temperature of from 300°C to 600°C.

[0072] The third aspect of the present invention will be described in further detail with respect to a case where propane is used as the starting material alkane and air is used as the oxygen source. The proportion of air to be supplied for the reaction is important with respect to the selectivity for the resulting acrylonitrile. Namely, high selectivity for acrylonitrile is obtained when air is supplied within a range of at most 25 moles, particularly 1 to 15 moles, per mole of the propane. The proportion of ammonia to be supplied for the reaction is preferably within a range of from 0.2 to 5 moles, particularly from 0.5 to 3 moles, per mole of propane. This reaction may usually be conducted under atmospheric pressure, but may be conducted under a slightly increased pressure or a slightly reduced pressure. With respect to other alkanes such as isobutane, or to mixtures of alkanes and alkenes such as propane and propene, the composition of the feed gas may be selected in accordance with the conditions for propane.

[0073] The process of the third aspect of the present invention may be conducted at a temperature of, for example, from 250°C to 480°C. More preferably, the temperature is from 300°C to 400°C. The gas space velocity, SV, in the gas phase reaction is usually within the range of from 100 to 10,000 hr⁻¹, preferably from 300 to 6,000 hr⁻¹, more preferably from 300 to 2,000 hr⁻¹. As a diluent gas, for adjusting the space velocity and the oxygen partial pressure, an inert gas such as nitrogen, argon or helium can be employed. When ammoxidation of propane is conducted by the method of the present invention, in addition to acrylonitrile, carbon monoxide, carbon dioxide, acetonitrile, hydrocyanic acid and acrolein may form as by-products.

Examples

Comparative Example 1

[0074] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_x$ was prepared in the following manner: In a flask containing 300.2g of water, 68.05g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 13.39g of ammonium metavanadate (Alfa-Aesar) and 20.36g of telluric acid (Aldrich Chemical Company) were dissolved upon heating to 70°C. After cooling to 40°C, 328.03g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 1.35 wt. % Nb and 7.53g oxalic acid (Aldrich chemical Company) was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain the precursor solid. The solid precursor was calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane, at various reaction temperatures. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/10/3 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 1.

Table 1

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|-------------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Comp. Ex. 1 | 3 | 375 | 48.4 | 59.7 | 28.9 |
| Comp. Ex. 1 | 3 | 380 | 52.8 | 56.9 | 30.1 |
| Comp. Ex. 1 | 3 | 385 | 58.2 | 51.9 | 30.2 |
| Comp. Ex. 1 | 3 | 390 | 60.6 | 47.4 | 28.7 |

Example 1

[0075] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{Ni}_{0.005}\text{O}_x$ was prepared in the following manner: 34.03g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 6.71g of ammonium metavanadate (Alfa-Aesar), 10.08g of telluric acid (Aldrich Chemical Company) and 0.29g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa-Aesar) were dissolved in 150.2g water upon heating to 70°C. After cooling to 40°C, 164.25g of an aqueous solution of niobium

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oxalate (Reference Metals Company) containing 1.35 wt. % Nb and 3.77g oxalic acid (Aldrich chemical Company) was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain the precursor solid. The solid precursor was calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane, at various reaction temperatures and/or reactor residence times. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/10/3 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 2.

Table 2

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 1 | 3 | 345 | 48.3 | 72.8 | 35.2 |
| Ex. 1 | 3 | 350 | 54.3 | 76.9 | 41.8 |
| Ex. 1 | 3 | 355 | 62.1 | 74.4 | 46.2 |
| Ex. 1 | 3 | 360 | 70.7 | 53.1 | 37.5 |
| Ex. 1 | 4.5 | 350 | 69.3 | 53.7 | 37.2 |
| Ex. 1 | 6 | 340 | 65.4 | 57.7 | 37.7 |

Example 2

[0076] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{Ni}_{0.01}\text{O}_x$ was prepared in the following manner: 34.03 g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 6.70 g of ammonium metavanadate (Alfa-Aesar), 10.09 g of telluric acid (Aldrich Chemical Company) and 0.554 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa-Aesar) were dissolved in 150.1 g water upon heating to 70°C. After cooling to 40°C, 164.17g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 1.35 wt. % Nb and 3.77g oxalic acid (Aldrich chemical Company) was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain the precursor solid. The solid precursor was calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane, at various reaction temperatures and/or residence times. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/10/3 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 3.

Table 3

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 2 | 3 | 340 | 42.3 | 70.9 | 30.0 |
| Ex. 2 | 3 | 348 | 49.1 | 72.7 | 35.6 |
| Ex. 2 | 3 | 352 | 56.2 | 70.5 | 39.6 |
| Ex. 2 | 3 | 357 | 61.2 | 66.5 | 40.7 |
| Ex. 2 | 3 | 362 | 67.4 | 67.3 | 42.4 |

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Table 3 (continued)

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 2 | 4.5 | 350 | 68.3 | 63.2 | 43.0 |
| Ex. 2 | 6 | 365 | 67.4 | 65.9 | 44.5 |

Example 3

[0077] The catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{Ni}_{0.01}\text{O}_x$ used in example 11 was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane, at various reaction temperatures and/or reactor residence times. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 4.

Table 4

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 3 | 4 | 340 | 55.5 | 71.7 | 39.8 |
| Ex. 3 | 3 | 350 | 65.3 | 68.4 | 44.6 |
| Ex. 3 | 3 | 360 | 71.2 | 67.2 | 46.5 |

Examples 4

[0078] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{Ni}_{0.04}\text{O}_x$ was prepared in the following manner: 34.01 g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 6.70 g of ammonium metavanadate (Alfa-Aesar), 10.08 g of telluric acid (Aldrich Chemical Company) and 2.226 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa-Aesar) were dissolved in 150.1 g water upon heating to 70°C. After cooling to 40°C, 164.03 g of an aqueous solution of niobium oxalate (Reference Metals Company) 1.35 wt. % Nb and 3.81g oxalic acid (Aldrich chemical Company) was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain the precursor solid. The solid precursor was calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/10/3 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 5.

Table 5

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 4 | 3 | 350 | 44.7 | 70.5 | 31.5 |
| Ex. 4 | 3 | 365 | 64.6 | 62.1 | 40.1 |

Comparative Example 2

[0079] In a flask containing 390g of water, 46.4g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 9.2g of ammonium metavanadate (Alfa-Aesar) and 13.9g of telluric acid (Aldrich Chemical Company) were dis-

solved upon heating to 80°C. After cooling to 20°C, 201.3g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 10.44 mmole/g of niobium was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 73g of a precursor solid. 25g of the solid precursor were calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10-20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 6.

Table 6

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|-------------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Comp. Ex. 2 | 3 | 360 | 30 | 46 | 14 |
| Comp. Ex. 2 | 3 | 370 | 38 | 50 | 19 |
| Comp. Ex. 2 | 3 | 390 | 67 | 40 | 27 |

Example 5

[0080] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Pd}_{0.04}\text{C}_x$ was prepared in the following manner: 13.47g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 2.68g of ammonium metavanadate (Alfa-Aesar), 4.03g of telluric acid (Aldrich Chemical Company) and 0.68g of $\text{Pd}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ (Alfa-Aesar) were dissolved in water upon heating to 80°C. After cooling to 20°C, 59.07g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 10.33mmole/g of niobium was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 28g of a precursor solid. This solid precursor was calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 7.

Table 7

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 5 | 3 | 350 | 27 | 71 | 19 |
| Ex. 5 | 3 | 370 | 40 | 66 | 27 |
| Ex. 5 | 3 | 380 | 56 | 60 | 34 |
| Ex. 5 | 3 | 400 | 65 | 34 | 22 |

Example 6

[0081] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Pd}_{0.01}\text{O}_x$ was prepared by mixing ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), ammonium metavanadate (Alfa-Aesar), telluric acid (Aldrich Chemical Company) and $\text{Pd}(\text{NO}_3)_2 \cdot \text{XH}_2\text{O}$ (Alfa-Aesar) in the appropriate ratios in water heated to 80°C. After cooling to 20°C, the right amount of an aqueous solution of niobium oxalate (Reference Metals Company) was mixed therewith

to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain the precursor solid. This solid precursor were calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 8.

Table 8

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 6 | 3 | 368 | 44.7 | 64.3 | 28.7 |
| Ex. 6 | 4.5 | 375 | 62.4 | 60.3 | 37.6 |
| Ex. 6 | 6 | 375 | 66 | 52.5 | 34.7 |

Example 7

[0082] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{O}_x$ was prepared in the manner as described in Example 1. Approximately 0.5g of the granules were packed into a quartz tube reactor for the gas phase oxidation of propane. The oxidation was conducted with a feed ratio of propane/steam/air of 1/3/96. The effluent from the reactor was analyzed by infra-red spectrometry (IR) to determine the propane conversion and the yield of acrylic acid. The results (along with residence time and reaction temperature) are shown in Table 9.

Table 9

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 7 | 3 | 280 | 12.1 | 44.5 | 5.4 |
| Ex. 7 | 3 | 330 | 33.2 | 41.6 | 13.8 |
| Ex. 7 | 3 | 350 | 46.0 | 32.6 | 15.0 |
| Ex. 7 | 3 | 370 | 59.3 | 20.9 | 12.4 |
| Ex. 7 | 3 | 380 | 65.9 | 16.2 | 10.7 |

Example 8

[0083] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Pd}_{0.04}\text{O}_x$ was prepared in the manner as described in Example 4. Approximately 0.5g of the granules were packed into a quartz tube reactor for the gas phase oxidation of propane. The oxidation was conducted with a feed ratio of propane/steam/air of 1/3/96. The effluent from the reactor was analyzed by infra-red spectrometry (IR) to determine the propane conversion and the yield of acrylic acid. The results (along with residence time and reaction temperature) are shown in Table 10.

Table 10

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 8 | 3 | 370 | 25 | 92 | 23 |
| Ex. 8 | 3 | 380 | 30 | 83 | 25 |
| Ex. 8 | 3 | 390 | 37 | 73 | 27 |
| Ex. 8 | 3 | 400 | 43 | 60 | 26 |

Comparative Example 3

[0084] 100 mL of an aqueous solution containing ammonium heptamolybdate tetrahydrate (1.0M Mo), ammonium metavanadate (0.3M V) and telluric acid (0.23 Te), formed by dissolving the corresponding salts in water at 70°C, was added to a 1000mL rotavap flask. Then 50mL of an aqueous solution of niobium oxalate (0.25M Nb) and oxalic acid (0.31M) were added thereto. After removing the water via a rotary evaporator with a warm water bath at 50°C and 28 mm/Hg, the solid materials were further dried in a vacuum oven at 25°C overnight and then calcined. (Calcination was effected by placing the solid materials in an air atmosphere and then heating them to 275°C at 10°C/min and holding them under the air atmosphere at 275°C for one hour; the atmosphere was then changed to argon and the material was heated from 275°C to 600°C at 2°C/min and the material was held under the argon atmosphere at 600°C for two hours.) The final catalyst had a nominal composition of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_f$. The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules for reactor evaluation.

Example 9

[0085] 50 mL of an aqueous solution containing ammonium heptamolybdate tetrahydrate (1.0M Mo), ammonium metavanadate (0.3M V) and telluric acid (0.23 Te), formed by dissolving the corresponding salts in water at 70°C, was added to a 1000mL rotavap flask. Then 25 mL of an aqueous solution of niobium oxalate (0.25M Nb) and oxalic acid (0.31M) and 1.25 mL of an aqueous solution of copper (II) nitrate hemipentahydrate (0.1M) were added thereto. After removing the water via a rotary evaporator with a warm water bath at 50 °C and 28 mm/Hg, the solid materials were further dried in a vacuum oven at 25°C overnight. This solid precursor were calcined by placing the solid materials in an air atmosphere and then heating them to 275°C at 10°C/min and holding them under the air atmosphere at 275°C for one hour; the atmosphere was then changed to argon and the material was heated from 275°C to 600°C at 2°C/min and the material was held under the argon atmosphere at 600°C for two hours. The final catalyst had a nominal composition of $\text{Cu}_{0.0025}\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_f$. The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules for reactor evaluation.

[0086] The catalysts of Comparative Example 3 and Example 9 were evaluated in a 10cm long Pyrex® tube reactor (internal diameter: 3.9mm). The catalyst bed (4cm long) was positioned with glass wool at approximately mid-length in the reactor and was heated with an electric furnace. Mass flow controllers and meters regulated the gas flow rate. The oxidation was conducted using a feed gas stream of propane, steam and air, with a feed ratio of propane : steam : air of 1 : 3 : 96. The reactor effluent was analyzed by an FTIR. The results (along with reaction temperature and residence time) are shown in Table 11.

Table 11

| Catalyst | Temperature (°C) | Residence Time (sec) | Propane Conversion (%) | Acrylic Acid Yield (%) |
|-------------|------------------|----------------------|------------------------|------------------------|
| Comp. Ex. 3 | 390 | 3 | 41 | 17 |
| Ex. 9 | 390 | 3 | 59 | 27 |

Comparative Example 4

[0087] 100 mL of an aqueous solution containing ammonium heptamolybdate tetrahydrate (1.0M Mo), ammonium metavanadate (0.3M V) and telluric acid (0.23 Te), formed by dissolving the corresponding salts in water at 70°C, was added to a 1000mL rotavap flask. Then 50mL of an aqueous solution of niobium oxalate (0.25M Nb) and oxalic acid (0.31M) were added thereto. After removing the water via a rotary evaporator with a warm water bath at 50°C and 28 mm/Hg, the solid materials were further dried in a vacuum oven at 25°C overnight and then calcined. (Calcination was effected by placing the solid materials in an air atmosphere and then heating them to 275°C at 10°C/min and holding them under the air atmosphere at 275°C for one hour; the atmosphere was then changed to argon and the material was heated from 275°C to 600°C at 2°C/min and the material was held under the argon atmosphere at 600°C for two hours.) The final catalyst had a nominal composition of $\text{Mo}_1\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_f$. The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules for reactor evaluation.

Example 10

[0088] 50 mL of an aqueous solution containing ammonium heptamolybdate tetrahydrate (1.0M Mo), ammonium metavanadate (0.3M V) and telluric acid (0.23 Te), formed by dissolving the corresponding salts in water at 70°C, was added to a 1000mL rotavap flask. Then 25 mL of an aqueous solution of niobium oxalate (0.25M Nb) and oxalic acid

(0.31M) and 1.25 mL of an aqueous solution of silver nitrate (0.1M) were added thereto. After removing the water via a rotary evaporator with a warm water bath at 50°C and 28 mm/Hg, the solid materials were further dried in a vacuum oven at 25°C overnight. This solid precursor were calcined by placing the solid materials in an air atmosphere and then heating them to 275°C at 10°C/min and holding them under the air atmosphere at 275°C for one hour; the atmosphere was then changed to argon and the material was heated from 275°C to 600°C at 2°C/min and the material was held under the argon atmosphere at 600°C for two hours. The final catalyst had a nominal composition of $\text{Ag}_{0.0025}\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.125}\text{O}_x$. The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules for reactor evaluation.

[0089] The catalysts of Comparative Example 4 and Example 10 were evaluated in a 10cm long Pyrex® tube reactor (internal diameter: 3.9mm). The catalyst bed (4cm long) was positioned with glass wool at approximately mid-length in the reactor and was heated with an electric furnace. Mass flow controllers and meters regulated the gas flow rate. The oxidation was conducted using a feed gas stream of propane, steam and air, with a feed ratio of propane : steam : air of 1 : 3 : 96. The reactor effluent was analyzed by an FTIR. The results (along with reaction temperature and residence time) are shown in Table 12.

Table 12

| Catalyst | Temperature (°C) | Residence Time (sec) | Propane Conversion (%) | Acrylic Acid Yield (%) |
|-------------|------------------|----------------------|------------------------|------------------------|
| Comp. Ex. 4 | 390 | 3 | 41 | 17 |
| Ex. 10 | 390 | 3 | 45 | 26 |

Comparative Example 5

[0090] In a flask containing 390g of water, 46.4g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 9.2g of ammonium metavanadate (Alfa-Aesar) and 13.9g of telluric acid (Aldrich Chemical Company) were dissolved upon heating to 80°C. After cooling to 20°C, 201.3g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 10.44 mmole/g of niobium was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 73g of a precursor solid. 25g of the solid precursor were calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmosphere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10-20 mesh granules. Approximately 0.5g of the granules were packed into a quartz tube reactor for the gas phase oxidation of propane. The oxidation was conducted with a feed ratio of propane/steam/air of 1/3/96. The effluent from the reactor was analyzed by infra-red spectrometry (IR) to determine the propane conversion and the yield of acrylic acid. The results (along with residence time and reaction temperature) are shown in Table 13.

Table 13

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|-------------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Comp. Ex. 5 | 3 | 280 | 12.1 | 44.5 | 5.4 |
| Comp. Ex. 5 | 3 | 330 | 33.2 | 41.6 | 13.8 |
| Comp. Ex. 5 | 3 | 350 | 46.0 | 32.6 | 15.0 |
| Comp. Ex. 5 | 3 | 370 | 59.3 | 20.9 | 12.4 |
| Comp. Ex. 5 | 3 | 380 | 65.9 | 16.2 | 10.7 |

Example 11

[0091] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Ag}_{0.04}\text{O}_x$ was prepared in the following manner: 13.58 g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 2.70 g of ammonium metavanadate (Alfa-Aesar), 4.06 g of telluric acid (Aldrich Chemical Company) and 0.51 g of $\text{Ag}(\text{NO}_3)_3$ (Alfa-Aesar) were dissolved in water upon heating to 80°C. After cooling to 20°C, 59.56 g of an aqueous solution of niobium oxalate (Reference Metals Company) containing 10.33mmole/g of niobium was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 28g of a precursor solid. This solid precursor were calcined in a quartz tube. (The quartz tube was placed in an oven under an air atmos-

phere, the oven was heated to 275°C and held there for one hour; a flow of argon (100cc/min) over the precursor material was then begun and the oven was heated to 600°C and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. Approximately 0.5g of the granules were packed into a quartz tube reactor for the gas phase oxidation of propane. The oxidation was conducted with a feed ratio of propane/steam/air of 1/3/96. The effluent from the reactor was analyzed by infra-red spectrometry (IR) to determine the propane conversion and the yield of acrylic acid. The results (along with residence time and reaction temperature) are shown in Table 14.

Table 14

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Selectivity (%) | Acrylic Acid Yield (%) |
|----------|----------------------|------------------|------------------------|------------------------------|------------------------|
| Ex. 11 | 3 | 323 | 3 | 100 | 3 |
| Ex. 11 | 3 | 337 | 4 | 100 | 4 |
| Ex. 11 | 3 | 349 | 7 | 71 | 5 |
| Ex. 11 | 3 | 357 | 8 | 63 | 5 |
| Ex. 11 | 3 | 371 | 11 | 64 | 7 |
| Ex. 11 | 3 | 382 | 15 | 47 | 7 |
| Ex. 11 | 3 | 392 | 19 | 42 | 8 |

Comparative Example 6

[0092] In a flask containing 215g of water, 25.68g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 5.06g of ammonium metavanadate (Alfa-Aesar) and 7.68g of telluric acid (Aldrich Chemical Company) were dissolved upon heating to 70°C. After cooling to 40°C, 122.94g of an aqueous solution of niobium oxalate (H. C. Starck) containing 1.25% Nb to which 2.84g of oxalic acid (Aldrich Chemical Company) had been added was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 46g of a precursor solid. 23g of this catalyst precursor solid was calcined in a quartz tube. (The quartz tube was placed in an oven with a 100 cc/min flow of air through the tube, the oven was then heated to 275°C at 10°C/min and held there for one hour; then using a 100 cc/min flow of argon through the tube, the oven was heated to 600°C at 2°C/min and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10-20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 15.

Example 12

[0093] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Au}_{0.01}\text{O}_x$ was prepared in the following manner: 12.93g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 2.55g of ammonium metavanadate (Alfa-Aesar), 3.87g of telluric acid (Aldrich Chemical Company) and 0.26g of ammonium tetrachloroaurate (Alfa-Aesar) were dissolved in water upon heating to 70°C. After cooling to 40°C, 67.37g of an aqueous solution of niobium oxalate (H. C. Starck) containing 1.25% Nb to which 1.43g of oxalic acid (Aldrich Chemical Company) had been added was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 28g of a precursor solid. This catalyst precursor solid was calcined in a quartz tube. (The quartz tube was placed in an oven with a 100 cc/min flow of air through the tube, the furnace was then heated to 275°C at 10°C/min and held there for one hour; then using a 100 cc/min flow of argon through the tube, the oven was heated to 600°C at 2°C/min and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a

gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 15.

Example 13

[0094] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Au}_{0.005}\text{O}_x$ was prepared in the following manner: 12.93g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 2.55g of ammonium metavanadate (Alfa-Aesar), 3.87g of telluric acid (Aldrich Chemical Company) and 0.13g of ammonium tetrachloroaurate (Alfa-Aesar) were dissolved in water upon heating to 70°C. After cooling to 40°C, 67.37g of an aqueous solution of niobium oxalate (H. C. Starck) containing 1.25% Nb to which 1.43g of oxalic acid (Aldrich Chemical Company) had been added was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 28g of a precursor solid. This catalyst precursor solid was calcined in a quartz tube. (The quartz tube was placed in an oven with a 100 cc/min flow of air through the tube, the furnace was then heated to 275°C at 10°C/min and held there for one hour; then using a 100 cc/min flow of argon through the tube, the oven was heated to 600°C at 2°C/min and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 15.

Example 14

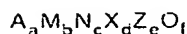
[0095] A catalyst of nominal composition $\text{Mo}_{1.0}\text{V}_{0.3}\text{Te}_{0.23}\text{Nb}_{0.08}\text{Au}_{0.0025}\text{O}_x$ was prepared in the following manner: 12.93g of ammonium heptamolybdate tetrahydrate (Aldrich Chemical Company), 2.55g of ammonium metavanadate (Alfa-Aesar), 3.87g of telluric acid (Aldrich Chemical Company) and 0.07g of ammonium tetrachloroaurate (Alfa-Aesar) were dissolved in water upon heating to 70°C. After cooling to 40°C, 67.37g of an aqueous solution of niobium oxalate (H. C. Starck) containing 1.25% Nb to which 1.43g of oxalic acid (Aldrich Chemical Company) had been added was mixed therewith to obtain a solution. The water of this solution was removed via a rotary evaporator at a temperature of 50°C and a pressure of 28mmHg to obtain 28g of a precursor solid. This catalyst precursor solid was calcined in a quartz tube. (The quartz tube was placed in an oven with a 100 cc/min flow of argon through the tube, the furnace was then heated to 275°C at 10°C/min and held there for one hour; then using a 100 cc/min flow of argon through the tube, the oven was heated to 600°C at 2°C/min and held there for two hours.) The catalyst, thus obtained, was pressed in a mold and then broken and sieved to 10 - 20 mesh granules. 10g of these granules were packed into a stainless steel U-tube reactor (inside diameter: 1.1cm) for the gas phase oxidation of propane. The U-tube reactor was placed in a molten salt bath and fed with a mixture of propane, air and steam having a feed ratio of propane/air/steam of 1/15/14 and having a space velocity of 1200 hr⁻¹. The effluent of the reactor was condensed to separate a liquid phase and a gas phase. The gas phase was analyzed by gas chromatography to determine the propane conversion. The liquid phase was also analyzed by gas chromatography for the yield of acrylic acid. The results (along with residence time and reactor temperature) are shown in Table 15.

Table 15

| Catalyst | Residence Time (sec) | Temperature (°C) | Propane Conversion (%) | Acrylic Acid Yield (%) |
|-------------|----------------------|------------------|------------------------|------------------------|
| Comp. Ex. 6 | 3 | 400 | 24 | 14 |
| Ex. 12 | 3 | 400 | 45 | 21 |
| Ex. 13 | 3 | 400 | 52 | 22 |
| Ex. 14 | 3 | 400 | 47 | 21 |

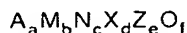
Claims

1. A catalyst comprising a promoted mixed metal oxide having the empirical formula



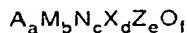
wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

2. The catalyst according to claim 1, wherein M is V, N is Te and/or Sb and X is Nb.
3. The catalyst according to claim 2, wherein A is Mo and N is Te.
4. A process for producing an unsaturated carboxylic acid, which comprises subjecting an alkane or a mixture of an alkane and an alkene to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing a promoted mixed metal oxide having the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 0.1 and f is dependent on the oxidation state of the other elements.

5. A process for producing an unsaturated nitrile, which comprises subjecting an alkane, or a mixture of an alkane and an alkene, and ammonia to a vapor phase catalytic oxidation reaction in the presence of a catalyst containing a promoted mixed metal oxide having the empirical formula



wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Sb, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au; and wherein, when $a = 1$, $b = 0.01$ to 1.0 , $c = 0.01$ to 1.0 , $d = 0.01$ to 1.0 , $e = 0.001$ to 1.0 and f is dependent on the oxidation state of the other elements.

6. A catalyst produced by the process comprising:

- (1) admixing compounds of the elements A, M, N, X and Z and at least one solvent to form an admixture, wherein A is at least one element selected from the group consisting of Mo and W, M is at least one element selected from the group consisting of V and Ce, N is at least one element selected from the group consisting of Te, Sb and Se, X is at least one element selected from the group consisting of Nb, Ta, Ti, Al, Zr, Cr, Mn, Fe, Ru, Co, Rh, Ni, Pt, Bi, B, In, As, Ge, Sn, Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, Ra, Hf, Pb, P, Pm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, and Z is selected from the group consisting of Ni, Pd, Cu, Ag and Au and wherein the elements A, M, N, X and Z are present in such amounts that the atomic ratio of A:M:N:X:Z is 1:0.01 to 1.0:0.01 to 1.0:0.001 to 0.1;
- (2) removing said at least one solvent from the admixture to obtain a catalyst precursor; and
- (3) calcining said catalyst precursor.

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7. The catalyst according to claim 6, wherein at least one of the compounds of the elements A, M, N, X and Z is an oxygen-containing compound.
8. The catalyst according to claim 6, wherein the admixture is a solution.
9. A process for producing an unsaturated carboxylic acid, which comprises subjecting an alkane or a mixture of an alkane and an alkene to a vapor phase catalytic oxidation reaction in the presence of the catalyst according to claim 6.
10. A process for producing an unsaturated nitrile, which comprises subjecting an alkane, or a mixture of an alkane and an alkene, and ammonia to a vapor phase catalytic oxidation reaction in the presence of the catalyst according to claim 6.



European Patent
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PARTIAL EUROPEAN SEARCH REPORT

Application Number

which under Rule 45 of the European Patent Convention shall be considered, for the purposes of subsequent proceedings, as the European search report

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.7) |
| D, X Y | US 5 231 214 A (UMEZAWA TIAKI ET AL) 27 July 1993 (1993-07-27) * column 1, line 52 - column 2, line 53; examples 2, 19 * | 1-3, 5-8, 10 4, 9 | B01J23/00 B01J23/28 B01J27/057 C07C253/24 C07C51/215 |
| X | US 6 063 728 A (KOMADA SATORU ET AL) 16 May 2000 (2000-05-16) * column 8, line 14 - line 47; claims 1-4 * | 1-3, 5-8, 10 | |
| X | EP 0 767 164 A (MITSUBISHI CHEM CORP) 9 April 1997 (1997-04-09) * page 2, line 46 - page 3, line 49 * | 1, 2, 5-8, 10 | |
| Y | EP 0 970 942 A (MITSUBISHI CHEM CORP) 12 January 2000 (2000-01-12) * claims 1-13 * | 4, 9 | |
| A | EP 0 404 529 A (NITTO CHEMICAL INDUSTRY CO LTD) 27 December 1990 (1990-12-27) * claims 1, 14 * | 1 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.7) |
| | | | B01J C07C |
| INCOMPLETE SEARCH | | | |
| <p>The Search Division considers that the present application, or one or more of its claims, does/do not comply with the EPC to such an extent that a meaningful search into the state of the art cannot be carried out, or can only be carried out partially, for these claims.</p> <p>Claims searched completely :</p> <p>Claims searched incompletely :</p> <p>Claims not searched :</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p> | | | |
| Place of search | | Date of completion of the search | Examiner |
| BERLIN | | 10 January 2002 | Cubas Alcaraz, J |
| CATEGORY OF CITED DOCUMENTS | | <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>Δ : member of the same patent family, corresponding document</p> | |
| <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> | | | |

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INCOMPLETE SEARCH
SHEET C

Application Number
EP 01 30 8131

Claim(s) searched completely:
2, 3

Claim(s) searched incompletely:
1, 4-10

Reason for the limitation of the search:

Present claims 1 and 4-10 relate to an extremely large number of possible catalyst compositions. Support within the meaning of Article 84 EPC and/or disclosure within the meaning of Article 83 EPC is to be found, however, for only a very small proportion of the catalyst compositions claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the catalyst compositions of claims 2 and 3.

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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10-01-2002

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US 5231214 A | 27-07-1993 | CN 1066445 A , B | 25-11-1992 |
| | | DE 69201995 D1 | 18-05-1995 |
| | | DE 69201995 T2 | 12-10-1995 |
| | | EP 0512846 A1 | 11-11-1992 |
| | | JP 3235177 B2 | 04-12-2001 |
| | | JP 5148212 A | 15-06-1993 |
| US 6063728 A | 16-05-2000 | JP 11047598 A | 23-02-1999 |
| | | DE 19835247 A1 | 11-02-1999 |
| | | EP 0895809 A1 | 10-02-1999 |
| | | US 6036880 A | 14-03-2000 |
| | | US 6143916 A | 07-11-2000 |
| | | JP 11239725 A | 07-09-1999 |
| EP 0767164 A | 09-04-1997 | CN 1155536 A , B | 30-07-1997 |
| | | DE 69603810 D1 | 23-09-1999 |
| | | DE 69603810 T2 | 16-03-2000 |
| | | EP 0767164 A1 | 09-04-1997 |
| | | JP 9157241 A | 17-06-1997 |
| | | US 5750760 A | 12-05-1998 |
| EP 0970942 A | 12-01-2000 | AU 4966197 A | 10-06-1998 |
| | | EP 0970942 A1 | 12-01-2000 |
| | | US 6166241 A | 26-12-2000 |
| | | WO 9822421 A1 | 28-05-1998 |
| EP 0404529 A | 27-12-1990 | JP 2950851 B2 | 20-09-1999 |
| | | JP 3026342 A | 04-02-1991 |
| | | DE 69012450 D1 | 20-10-1994 |
| | | DE 69012450 T2 | 02-03-1995 |
| | | EP 0404529 A1 | 27-12-1990 |
| | | ES 2063920 T3 | 16-01-1995 |
| | | US 5094990 A | 10-03-1992 |

EPO FORM 0442

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82